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Present and Future Status of  
Organic Analytical Reagents – Part IV

# ORGANIC ANALYTICAL REAGENTS IN ATOMIC ABSORPTION SPECTROPHOTOMETRY OF METALS

*Prepared for publication by*

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# Present and future status of organic analytical reagents – Part IV. Organic analytical reagents in atomic absorption spectrophotometry of metals (Technical Report)

## Abstract

The effects of frequently used organic analytical reagents (OARs) in flame and electrothermal atomic absorption spectrophotometry (AAS) are surveyed. The sensitivity and selectivity of the AAS determinations of some elements are increased and the matrix effects suppressed or diminished in the presence of appropriate OARs. The mechanisms for the various effects observed with OARs are discussed. Examples are given of the beneficial use of OARs in both flame and electrothermal AAS.

## 1. INTRODUCTION

Results in AAS may be affected by organic analytical reagents (OARs) in various ways. OARs may interact with a species of an element in solution forming complexes of differing stabilities and be active during all the main steps of an AAS procedure, i.e. (a) nebulization of sample solution, (b) drying of aerosol droplets, or of analyte solution films on solid atomizer surfaces, (c) thermal decomposition (pyrolysis, charring) and, (d) atomization. The signal enhancement from OARs in AAS is due to improvement of atomization efficiency of elements resulting in increase of sensitivity of determinations or by *diminishing or even removing interferences from matrix components*. OARs are often suitable as releasing agents or matrix modifiers; however, in some instances negative effects are observed. The effects, positive or negative, during the AAS determination of metals depends on the particular mechanism of thermal decomposition of the analyte-OAR species, the atomization mechanism and the kind of interaction with accompanying elements (1, 2). Solvents may be considered as a special type of OAR, their interaction may be multifaceted but is normally of a physical character *via* surface tension, viscosity and latent heat effects. However, examples of reactive solvents are known such as trichlorotrifluoroethane used for fluoride evolution in the determination of silicon (3).

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### 1.1 The main factors to be considered in the discussion of the effects of OARs in flame and flameless AAS

(a) An OAR metal complex may evaporate after desolvation or sublime without decomposition during thermal treatment (pyrolysis) and then dissociate to give free atoms to cause the absorption signal. However, an analyte loss may result from evaporation or sublimation at temperatures lower than the atomisation temperature resulting in a decrease of the atomic absorption signal. In flames, the OAR complex volatilizes into a medium of higher temperature than that of the aerosol particles. In solid atomizers the volatilization usually takes place into a cooler medium in comparison to that of the atomizer surface. In addition, complicated interactions such as carbide formation of the analyte, may take place with or on the atomizer surface.

(b) The product of decomposition of the analyte complex with a particular OAR depends on the type of metal-donor atom bond. Complexes containing M-O bonds normally decompose to oxides, those with M-N bonds to elemental metal, and those with M-S bonds to sulfides (4,5). If an oxide or elemental metal is formed during decomposition the atomization mechanism is similar to that of simple inorganic salt analytes. No clear relations have been established between complexation stability in the nebulised or applied solutions and the overall effect of particular OARs during AAS (1).

(c) The pyrolysis of organic material may lead to molecular fragments or to highly reducing elemental carbon which enhance the atomization of oxides. The absorption signal is, however, decreased when thermostable metal carbides are formed, both in the gaseous and condensed phases, in the presence of OARs. The resultant effect is governed by the differences between the volatilities and stabilities of the particular metal oxide and carbide (6).

(d) An OAR may protect the analyte against the formation of thermostable ternary species, especially in flames, or in samples with complicated matrices, and thus eliminate their effects. In electrothermal AAS OARs often change the mechanism of the metal ion interaction with the atomizer surface, as well as removing the overlap in time of analyte and matrix evaporation (1,2).

(e) If the OAR-analyte species is in an organic solvent, the nebulization efficiency may be solvent dependant. In a solid atomizer organic solvents can change the location and area covered by the sample on the atomizer surface. Solvent vapours or their decomposition fragments may interfere with the charring and the atomization steps (2,3,7-10).

## 2. OARs IN FLAME AAS

### 2.1 Nebulization

The formation of small, relatively uniform discrete droplets which evaporate rapidly producing dry aerosol particles is required for high sensitivity. This stage is very important to the subsequent atomization process and may be influenced by OARs and by solvents (10). The addition of an inert

gas of high thermal conductivity, such as helium, to a flame leads to faster evaporation of droplets and to enhanced atomization (11). Nitrogen formed from the thermal decomposition of hydrazine assists the fragmentation of droplets and thereby produces smaller aerosol particles that vapourise more readily (11).

The presence of long-chain surfactants decreases the surface tension values of aqueous solutions but does not produce the expected modification of characteristics of pneumatically generated aerosols. This has been attributed to hydrodynamic effects during the very short period of time required for nebulization. Surface active molecules require significant time to migrate to the surface before they affect surface tension (12).

Oxygenated solvents such as aliphatic ketones (commonly, methyl isobutyl ketone), aliphatic alcohols or esters, or their mixtures with xylene (13) are suitable for the direct nebulization of analyte-OAR extracts into flames or for the study of sparingly water soluble OAR-analyte species. The enhancement of AAS sensitivity for a range of solvents has been correlated with their physical properties, namely, surface tension, viscosity and boiling point (14).

## 2.2 Vapour phase sample introduction

The direct introduction of volatile metal chelates or of organometallic compounds in flame AAS avoids the losses and other problems associated with pneumatic nebulization. A variety of cobalt chelates have been examined for the analysis of steels, bronzes and brasses; trifluoroacetylacetone was the preferred ligand (15). Variation in volatility may permit speciation of organometallic species in admixture, as has been found for tetramethyllead and tetraethyllead in gasolines (16).

## 2.3 Thermal decomposition of OAR-metal complexes

Gaseous metal atoms may be formed by dissociation or by reduction of metal oxides, carbides, nitrides, sulphides, halides, volatile metal complexes or organometallic species in the condensed or gaseous phase. The decomposition products of excess of OAR may protect free atoms against subsequent reactions in the flame. In flames, metal oxides mainly result from chelate decomposition and the subsequent atomization process is similar to that of inorganic salts (17,18). When metallocenes of  $Ti^{IV}$ ,  $Hf^{IV}$ ,  $Zr^{IV}$ ,  $Nb^V$  and  $Ta^V$  are nebulized, high atomization yields and sensitivities result, since refractory oxides are not formed when metallocene M-C bonds decompose (19,20). The absorption signal from molybdenum cyclo-pentadienyl tricarbonyl dimer is decreased compared to that from an equivalent amount of molybdenum present as molybdate since the close contact between the cyclopentadienyl ring and the metal atom in this sandwich structure aids the formation of non-volatile molybdenum carbide (21). Zirconium(IV), titanium(IV) and hafnium(IV) show enhanced AAS signals in a nitrous oxide-acetylene flame in the presence of nitrogen containing Lewis bases which prevent the formation of the polymeric oxyzirconium species (22). Atomization efficiency is also enhanced for

elements whose OAR compounds form easily dissociable metal sulphides during decomposition. There is, for example, a considerable relative increase of absorption signals for molybdenum when nebulized as its 3,4-toluene-dithiolate as compared to the equivalent amounts of its 8-hydroxyquinolate, cupferrate or acetylacetonate (23).

The composition, stoichiometry and temperature of flames are key factors in deciding the influence of an OAR on the sensitivity of AAS determinations. Flames containing C-radicals permit the reduction of oxides to free metal atoms (24-27). For example, the absorption signals in propane-air flames decreases in the presence of 8-hydroxyquinoline or EDTA; this effect is not observed in the hotter acetylene-air flame (28). Aliphatic amines which form stable complexes with Fe(III), Ni(II), or Co(II) are not completely decomposed in acetylene-air flames, whereas decomposition is complete in acetylene-nitrous oxide flames (29). Similarly, a decrease of the absorption signal was observed for silver in cool flames compared to hot flames in the presence of aliphatic amines and other ligands (30).

Metal-OAR complexes may also evaporate from the dry aerosol particles without decomposition and later dissociate, so that the sensitivity of an AAS determination is increased. For example, the atomization yield for titanium increases in acetylene-nitrous oxide flames in the presence of formic, acetic and propionic acids. The rapid evaporation of volatile  $Ti^{IV}$  complexes prevents the slow reduction of titanium(IV) species to metal or to titanium carbide of very low volatility (31,32). Similarly, the ready evaporation of chelates of  $Cu^{II}$ ,  $Co^{II}$ ,  $Fe^{III}$ ,  $Mn^{II}$ ,  $Ni^{II}$  and  $Zn^{II}$  with sodium diethyldithiocarbamate, 8-hydroxyquinoline, or acetylacetone from a tantalum boat in air acetylene flames gives rise to AAS sensitivity increases, in comparison with their simple inorganic salts (17,33,34).

#### **2.4 The effect of free carbon formed from OARs**

Free carbon produced during the preliminary heating processes in the condensed or gaseous phases, either in the form of radicals or in elementary form, may change the properties of the flame (14). The decomposition products of OARs have considerable reducing power which enhance the formation of analyte atoms in the gaseous state. Decomposition products including free carbon may, however, cause negative effects if less volatile metal carbides or elemental metal are produced in the condensed phase. Such effects are particularly noticeable for niobium, tantalum and molybdenum. The atomization yield increases when the metal or the metal carbide is more volatile than the corresponding oxide, as with aluminium and beryllium (5). Sulphonated aromatic compounds such as 5-sulphosalicylic acid (35) have been found to slightly increase the sensitivity of AAS determination of aluminium, beryllium and calcium, but considerably decrease the sensitivity for molybdenum, tungsten, vanadium and titanium whose carbides are less volatile than their oxides (32,35,36).

Tantalum(V) and uranium(VI) also give species of low volatility in the presence of 5-sulphosalicylic acid. The reduction in the AAS signal by aromatic sulphonic acids on titanium, molybdenum, tungsten and vanadium may be removed by addition of sodium or potassium salts. In their presence the aromatic sulphonic acids are converted in flames to sulphates which then transform the carbides or metals to oxides which dissociate or are reduced to gaseous metal atoms. Complexation is not important since naphthalene-1,5-disulphonic acid, which does not form complexes in solution with titanium, for example, has the same effect in flames as chromotropic acid (1,8-dihydroxynaphthalene 3,6-disulphonic acid) which forms stable  $Ti^{IV}$  chelates in solution (32).

### 2.5 OARs as releasing agents

The interfering effect of accompanying elements often results in the formation of non-volatile thermostable mixed oxides in the pre-atomization stage which do not produce free gaseous atoms in flames. An OAR in such cases may suppress the interferences in acetylene-air and other flames by chelating the interferent, the analyte, or both (37,38,39). Some typical examples are given in Table 1.

**Table 1. Selected OARs as releasing agents**

	Element to be determined determined	Interferent whose effect is removed	Reference
8-Hydroxy-quinoline	Cr	Ti, Fe, V	37
	Mg, Ca	Al, Ti, Zr, Be	38, 39
	Ba, Be	Al	40, 41
	Co	$PO_4^{3-}$	42
	Fe	Co, Ni, Cu	43
5-Sulfosalicylic acid	Mg	Si, Al, Ti, Zr, Be	38, 39
	Ca	$SO_4^{2-}$ , $PO_4^{3-}$ , Si, Ti, Zr, Be	38, 39
	Cr	Al	44
	Al	Si	44
	Fe	Ti	44
EDTA	Mg	Be	38
	Mn, Cu, Ni	V, Fe	45

The effect of addition of complexing agents can be rationalised, due to the formation of complexes with the analyte or the interferent, the analyte is protected from interactions with the interferent which hinders the formation of mixed oxides. The compactness of aerosol particles is disrupted during the decomposition and combustion of chelated and non-chelated organic compounds in the flame. This increases the surface area of particles, creates a reducing atmosphere around the analyte or accompanying elements and also breaks contact between both species which prevents the formation of thermostable ternary species (20,46,47). The efficiency of a particular OAR is often enhanced by the presence of lanthanum or strontium salts primarily added to deal with anion effects such as from phosphate.

### 3. OARs IN ELECTROTHERMAL AAS

The duration and temperature of the various stages from sample introduction to atom production, i.e. drying, pyrolysis (charring) and atomization can be easily programmed for electrothermal (solid) atomizers. The interaction of the sample with the atomizer surface, especially when it is made of graphite, can seriously influence the atomization process. Incomplete evaporation of the analyte may arise because of carbide formation since certain metal carbides are non-volatile even at 3000K. Lamellar graphite compounds can also be formed. The use of graphite tubes coated with pyrolytic graphite or with metal carbides such as those of Ta<sup>IV</sup>, Nb<sup>IV</sup>, Zr<sup>IV</sup>, W<sup>IV</sup>, and Mo<sup>IV</sup> prevent or diminish these interferences (48-50). Metallic atomizers, especially tungsten (51,52) may be advantageous for elements forming thermostable carbides. In addition, both higher temperatures (e.g. 3500K for W atomizers) and heating rates (30K/ms) can be achieved with metal atomizers compared to those made of graphite.

#### 3.1 Phenomena on the curvette surface after sample addition

The spreading of the sample solution on the atomizer surface depends on the physical properties of the solution being sampled (7). Variation in the structure and position of the samples can have a significant effect on measured absorption signals due to the steep temperature gradient along the graphite tube (9). Some OARs such as ascorbic acid and sucrose improve the placement of the analyte sample solution on the surface by decreasing diffusion of the sample into the bulk of the atomizer (53), as does saturation with OARs (54). The addition of the surfactant Triton X-100 to blood samples improves their adhesion to graphite surfaces and thus aids reproducibility of results (55).

Sample solutions containing organic solvents show rather complicated effects in electrothermal AAS. The earlier expectations that determinations using solid atomizers would be less dependent on the properties of the solvents than for AAS in flames has not been fulfilled. There are significant differences in calibration plots as between organic and aqueous solutions. The solvent effects depend

on the type of solvent and the nature of the atomizer surface. These include the position in time, the shape, height, width and splitting (if any) of the absorption signal (7, 56, 57). Peak splitting may indicate the formation of graphitic lamellar compounds as with  $\text{Fe}^{\text{III}}$  or  $\text{Cu}^{\text{II}}$  in the presence of halogenated solvents (17,58). In addition, the porosity of the graphite or presence of graphite powder influences the absorption signal (17). Double peaks have also been found in the analysis of organotin compounds in the presence of hexane due, it was considered, to the production of active carbon leading to two atomizing species (59). The extraction and atomization of volatile chlorides, e.g.  $\text{Ge}^{\text{IV}}$  (60) and the formation of volatile halo-organometallic compounds *via* ligand decomposition, e.g. for zinc (61) depresses absorption signals. Reduction in signals caused by halogenated solvents, compared the use of aqueous solutions in graphite atomizers is diminished by coating the graphite surface with tungsten carbides, e.g. for various dithiocarbamates of  $\text{Ni}^{\text{II}}$  (62) or using a tantalum boat within the graphite tube, e.g. for iron(III) and cobalt(II) (58,63).

### 3.2 Volatilization of metal chelates

Volatilization of metal OAR chelates, followed by rapid atomization in the gas phase, which would prevent losses, has not been observed for solutions directly sampled into a graphite tube. Increase of atomization efficiency is only possible by transfer of gaseous metal chelates into an atomizer preheated to the atomization temperature. Volatilization of metal OAR chelates during charring may cause losses and negative errors in the subsequent atomization and AAS determination. The volatility of a species depends on the design of the atomizer, the nature of its surface and on the solvent used in the sample solution. Chelates may evaporate along with the solvent as was found for thallium (64) and for selenium (65) dithiocarbamates in the presence of methyl isobutyl ketone. Losses of tin were observed when present as diethyldithiocarbamate or 8-hydroxyquinolate (66).

### 3.3 Thermal decomposition of metal chelates

The nature and stability of the metal-donor atom bonds in OAR complexes used in AAS determinations control the preatomization processes in the condensed phase such as the formation of oxides, carbides, sulphides, free metal or volatilization of unchanged metal chelates. The decomposition of OAR chelates containing sulfur donor atoms leads to the formation of metal sulfides or oxosulfides (5,17,67). The metal sulfides or oxosulfides then dissociate to free atoms or are reduced by carbon from the graphite tube (or OAR residues), or by hydrogen premixed with argon as used with molybdenum metal atomizers. Atomization mechanisms differing from the metal oxide scheme may cause a relative increase, e.g. for copper, cobalt and mercury on graphite or tantalum surfaces (5, 17, 63, 68, 69) or decrease, e.g. for lead and cadmium due to the formation of sulfides in the preatomization step. This effect can be diminished by the addition of oxygen to the argon carrier gas during charring (70, 71). The addition of thiourea increases the sensitivity of determination of Pt, Tl, Cu,



Mn, Bi, Cd and Hg, using a molybdenum atomizer and also overcomes peak splitting and shifts in time (67,72-75). In a graphite tube thiourea enhances the absorption signal for copper but decreases that for lead. This latter effect may be overcome by coating the graphite surface with molybdenum carbide which retains the sulfur (76). Some volatile elements are stabilised by formation of chelates, e.g. gallium by nitrosophenylhydroxylamine (77) and mercury by diethylthiocarbamate or dithizone (68,69).

### 3.4 Effect of carbon produced by OAR decomposition

Carbon produced by the thermal decomposition of OARs may enhance the carbothermic reduction of metal oxides in the gas phase as for cadmium and zinc, or in the solid phase as for lead and bismuth as in the presence of Na<sub>2</sub>EDTA (54). The interaction with carbon is especially important for elements forming stable oxides in the gas phase such as tin (66). The enhanced carbothermic reduction of oxides shifts the atomization signals to lower temperatures. Such shifts are observed for Pb, Zn, Cd, Bi, Ag and Hg in the presence of EDTA, for Pb and Zn in the presence of ascorbic acid, and for Hg in the presence of nitric and oxalic acid with accompanying increases in sensitivity for AAS determinations (57,78-83). Amino acids have been found to improve the sensitivity of Au determinations (84). The decomposition of OARs in chelates and when in excess as matrix modifiers increases the number of active centres on the graphite surface which play a considerable role during the atomization of Bi, Ca, Cd, Cr, Mn, Pb or Zn from graphite surfaces in the presence of ascorbic acid (78) or EDTA (79). Improved sensitivity can also be explained in terms of gas phase reactions. Hydrogen and carbon monoxide formed in the decomposition of ascorbic acid decrease the partial pressure of oxygen which changes the equilibrium position of oxide dissociation reactions (86,86). The absorption signal for tellurium decreases in the presence of glucose or ascorbic acid (87), as does that of vanadium in the presence of *N*-benzoyl-*N*-phenyl-hydroxylamine, dithiocarbamate and 8-hydroxyquinoline, even in a tungsten atomizer due to ease of carbide formation (88). Carbide formation can be avoided by fluoridation from the addition of polytetrafluoroethylene to refractory metal samples prior to, for example, electrothermal vapourization for determination by inductively coupled plasma atomic emission spectrometry (89).

### 3.5 OARs as matrix modifiers

The chemical and physical properties of the sample matrix may be changed by the presence of specially added inorganic or organic species which result in differentiation of analyte and matrix evaporation as the temperature is raised. Matrix elements or components may cause:

- (a) losses of analyte prior to atomization;
- (b) formation of molecular species in the gas phase or of stable compounds in the solid phase;
- (c) occlusion of the analyte in the matrix during electrothermal AAS.

The cause of the effect of a matrix modifier is not always well understood, since both analyte and interferences often form complexes with the modifier. Some useful examples of OAR matrix modification are given in Table 2. Excess of nitric acid often affects absorption signals negatively which is explained by destruction of the surface of the graphite tube and incorporation of the analyte into the graphite structure (53). This effect can be overcome by the prior transformation of the analyte into an OAR chelate, for example, nickel with dimethylglyoxime (90). The mutual interaction of bismuth, copper and cadmium in a molybdenum atomizer with formation of thermostable intermetallic compounds can be overcome *via* sulfide formation by addition of thiourea. Various OARs, especially EDTA, lower atomization temperatures of elements such as Cd, Zn, Bi, Pb, Ag and Hg which enables a better separation of the analyte signal from that of the non-volatile sample matrix (81,82). Ascorbic acid acts as a matrix modifier in the determination of tin in excess boric acid by formation of involatile boron carbide (91).

**Table 2. Elimination of matrix effects by OAR modifiers**

Analyte	Matrix	OAR	Reference
Au	NaCl	cysteine	84
Bi <sup>a</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , Pb(NO <sub>3</sub> ) <sub>2</sub> , AgNO <sub>3</sub>	thiourea	96
Cd	NaCl, seawater	mercaptoacetic, nitrilotriacetic, citric, lactic, ascorbic, aspartic acids, EDTA, glucose, cysteine, nitrilotriethanol, arginine, histidine creatinine, ethylenediamine	80-82
Cd <sup>a</sup>	NaCl, Pb(NO <sub>3</sub> ) <sub>2</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , Bi(NO <sub>3</sub> ) <sub>3</sub>	thiourea	67,96
Cr	CaCl <sub>2</sub> , SrCl <sub>2</sub> , BaCl <sub>2</sub> , CuCl <sub>2</sub> , FeCl <sub>3</sub> , MgCl <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> EDTA, (NH <sub>4</sub> ) <sub>3</sub> citrate, (NH <sub>4</sub> ) <sub>2</sub> tartrate	95
Cu	NaCl, seawater	ascorbic acid	97
Cu <sup>a</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub> , Bi(NO <sub>3</sub> ) <sub>3</sub>	thiourea	96
Hg	NaCl	citric, ascorbic, oxalic acids, EDTA	83
Pb	NaCl, seawater	ascorbic acid	97
Pb	MgCl <sub>2</sub> , NaCl	ascorbic, adipic, maleic acids	98,99
Pb	NaCl, Bi(NO <sub>3</sub> ) <sub>3</sub>	thiourea	59,96
Zn	MgCl <sub>2</sub> , seawater	ascorbic acid	67,83

<sup>a</sup>molybdenum atomizer

Palladium is a useful chemical modifier to increase atomization temperature *via* formation of analyte-palladium alloys (82). The addition of ascorbic acid to palladium salts, as reducing agent, has been found to improve performance for the determination of selenium (92, 93, 94), and thallium (92). The interference of metal chlorides may be removed by addition of nitric and organic acids, or their ammonium salts. For example, the interference of copper chloride during the AAS determination of chromium decreases in the order  $(\text{NH}_4)_2\text{EDTA} > \text{H}_2\text{SO}_4 > (\text{NH}_4)_2 \text{ tartrate} > (\text{NH}_4)_3 \text{ citrate} > \text{HNO}_3$ . Chloride is removed by volatilization of hydrochloric acid or ammonium chloride and the analyte salt decomposed to its oxide. The highest efficiency is shown by  $(\text{NH}_4)_2\text{EDTA}$ , which can be explained in terms of the intermediate formation of stable water soluble metal EDTA chelates (95). The crystal structure of salts may also be disturbed during the evaporation of solutions containing a particular OAR. This effect allows OARs which do not enhance the atomization from pure analyte solutions to behave as matrix modifiers. For example, histidine has no effect on the atomization of cadmium from cadmium(II) chloride in deionized water, but enhances the signal in the AAS determination of cadmium for sea water (81).

## CONCLUSION

The effects of OARs on the atomization processes and hence on the absorption signals of analytes are complicated in nature and depend on the structure and properties of the OARs involved, the type of atomizer (flame, graphite, metal), and the analyte itself. In many cases, by careful selection of an appropriate OAR, the sensitivity and selectivity of analyte determinations by flame or by electrothermal AAS are increased and matrix effects eliminated or diminished. The stability and volatility of an analyte complex with a particular OAR, the type of metal-ligand bonding, the decomposition mechanism of the complex, and the atomization scheme of the analyte have to be considered in the selection of an appropriate OAR. In addition, any non-specific interactions of decomposition fragments of OARs, particularly carbon, play important roles either improving the reduction of analyte to free atoms (positive effects of OARs) or by the formation of thermostable carbides (negative effect of OARs). The formation of individual metal complexes with OARs may eliminate the formation of thermostable ternary species and thus decrease interferences during AAS determinations from complicated matrixes. Changes in the timing, position and shape, including splitting of the absorption signals in the presence of OARs, including solvents, are of special interest if biological, clinical or other complex matrixes are to be analysed by flameless AAS.

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